

PATENT APPLICATION

METHODS FOR PRODUCING LOW-K CDO FILMS

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CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application is related to US Patent Application No. 10/789,103 [Attorney Docket NOVLP094], filed on February 17, 2004, naming Wu et al. as inventors and titled "METHODS FOR PRODUCING LOW-K CDO FILMS WITH LOW RESIDUAL STRESS," which claims priority from US Provisional Patent Application No. 60/524,330, filed on November 20, 2003, naming Wu et al. as inventors and title "METHODS FOR PRODUCING LOW-K CDO FILM OF LOW RESIDUE STRESS WITH DIELECTRIC CONSTANT <3.0 ," both of which are incorporated herein by reference for all purposes.

FIELD OF THE INVENTION

[0002] This invention relates to methods for preparing dielectric films having low dielectric constants and high mechanical strength.

BACKGROUND

[0003] There is a general need for materials with low dielectric constants (low-k) in the integrated circuit manufacturing industry. Using low-k materials as the interlayer dielectric of conductive interconnects reduces the delay in signal propagation and signal crosstalk due to capacitive effects. The lower the dielectric constant of the dielectric, the lower the capacitance of the dielectric and the RC delay in the lines and signal crosstalk between electrical lines of the IC. Further, the use of low k materials as interlayer dielectrics will reduce power consumption of complex integrated circuits.

[0004] Low-k dielectrics are conventionally defined as those materials that have a dielectric constant (k) lower than that of silicon dioxide (SiO_2), that is $k < \sim 4$. Generally, they have a dielectric constant of 3 or less. Typical methods of obtaining low-k materials include introducing pores into the dielectric matrix and/or doping silicon dioxide with various hydrocarbons or fluorine. In technology nodes of 90 nanometers and beyond (e.g., 65 nanometers), carbon doped oxide dielectric materials look extremely promising. However, wide spread deployment of these materials in modern integrated circuit fabrication processes is hindered by increasing demands for high mechanical strength coupled with lower dielectric constants. For certain applications, it is now necessary to use dielectric materials having k values below about 2.7.

SUMMARY

[0005] In one aspect of the invention, a carbon doped oxide (CDO) film containing carbon-carbon double bonds or carbon-carbon triple bonds or both is applied to a substrate by contacting the substrate with one or more CDO precursors having a carbon-carbon double bond, a carbon-carbon triple bond, or both. Because of the choice of precursors, the resulting film will have good mechanical properties while possessing a dielectric constant of not greater than about 2.7. In some implementations of the invention, the CDO film serves as an interlayer dielectric in an integrated circuit.

[0006] In a specific embodiment, the invention provides a method of preparing a carbon doped silicon oxide (CDO) film on a substrate. The method may be characterized by the following sequence: (a) providing the substrate to a deposition chamber; and (b) contacting the substrate with one or more CDO precursors, at least one of which contains some degree of unsaturation (e.g., a carbon-carbon triple bond or a carbon-carbon double bond). The method is conducted under process conditions in which the CDO film contains carbon-carbon triple bonds and has a dielectric constant of at most about 2.7 (preferably not greater than about 2.6). In some embodiments of commercial importance, the substrate is a partially fabricated integrated circuit, and the CDO film is, for example, interlayer dielectric.

[0007] Regarding the as deposited CDO film, preferably it has a carbon-carbon triple bond to silicon-oxygen bond ratio of about 0.05% to 20% based on FTIR peak areas. Typically, the film will also include derivative bond structures of carbon-carbon triple bonds such as carbon-carbon double bonds, carbon-carbon single bonds, and their crosslinked forms within the Si-O-Si matrix.

[0008] Many precursors and process gas compositions will be suitable for this invention. One or multiple CDO precursors may be employed. If only a single CDO precursor is employed, then it should include an unsaturated group (e.g., a carbon-carbon triple bond). In a specific embodiment, a single CDO precursor is a silane having at least one hydrocarbon group with a triple bond and at least one alkyl group or a bis(alkylsilyl)acetylene. A more specific set of examples includes ethynyltrimethylsilane (ETMS), propargyltrimethylsilane (PTMS),

propargyloxytrimethylsilane (POTMS), bis(trimethylsilyl)acetylene (BTMSA), 1,3-diethynyltetramethyldisiloxane (DTDS), dimethylmethoxysilaneacetylene (DMMOSA), methylmethoxysilaneacetylene (MDMOSA), dimethylethoxysilaneacetylene (DMEOSA), methyl-diethoxysilaneacetylene (MDEOSA), ethyl-diethoxysilaneacetylene (EDEOSA), and dimethylsilane-diacetylene (DMSDA).

[0009] For CDO deposition, the process gas should include a source of carbon, oxygen, silicon, and hydrogen. These elements can be found in the carrier gas, the precursor(s), and/or a separate oxidizer. In cases where at least two different precursors are employed, the primary CDO precursor may be an alkylsiloxane and the secondary CDO precursor may include the carbon-carbon triple bond. The secondary precursor may also include a carbon-carbon double bond. Examples include 1,3-divinyltetramethyldisiloxane (DVDS), vinyltrimethylsilane (VTMS), vinylmethylmethoxysilane (VMDMOS), and divinylmethoxysilane (DVDMS). Specific examples of carrier gases include carbon dioxide, oxygen, ozone, nitrous oxide, hydrogen peroxide, helium, argon, and other inert gases.

[0010] Another aspect of this invention pertains to integrated circuits having a carbon doped silicon oxide (CDO) dielectric layer containing carbon-carbon triple bonds and having a dielectric constant of not greater than about 2.7 (preferably not greater than about 2.6). In many embodiments, the CDO dielectric layer serves as an interlayer dielectric in the integrated circuit. And frequently the integrated circuit contains multiple CDO dielectric layers, each having carbon-carbon triple bonds.

[0011] In addition to having a low dielectric constant, the CDO film preferably has robust mechanical properties. For example, the film preferably has a cracking threshold of greater than 3 micrometers. Also, the film may have a modulus of not less than about 3 MPa.

[0012] These and other features and advantages of the invention will be presented in more detail below with reference to the associated drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

[0013] Figure 1 is a diagram of four major structural configurations for carbon in CDO films.

[0014] Figure 2 is a flowchart illustrating the basic method for creating low-k CDO dielectric layers with low residual stress and high hardness/modulus.

[0015] Figures 3a and 3b are Raman analysis graphs comparing a film prepared with TMCTS and a film prepared with BTMSA, respectively.

[0016] Figure 4A shows FTIR spectra of ETMS, OMCTS and OMCTS+ETMS films.

[0017] Figure 4B shows FTIR spectra of TMCTS and TMCTS and ETMS films.

[0018] Figure 5 shows the effect of BTMSA flow rate on dielectric constant.

[0019] Figure 6 is a graph illustrating how dielectric constant of deposited CDO films varies as a function of chamber pressure during deposition.

[0020] Figure 7 shows the dielectric constant and refractive index versus wafer number (repeatability).

[0021] Figure 8 provides a simple block diagram depicting various reactor components arranged as in a conventional reactor.

DETAILED DESCRIPTION OF A PREFERRED EMBODIMENT

INTRODUCTION AND OVERVIEW

[0022] The present invention relates to methods of creating low-k carbon doped oxide (CDO) layers with high mechanical strength and low residual stress. Generally, CDO film refers to a material whose compositional elements include Si, O, C and H. It may contain traces of other elements, including fluorine (F) or germanium (Ge). “Low-k”, in the context of this invention means that the dielectric constant of the CDO layer is not greater than about 3.5 and preferably not greater than about 2.7. In particularly preferred embodiments, the CDO layer has a dielectric constant of at most about 2.6.

[0023] It has been found that rigid chemical bonds such as carbon-carbon double bonds and carbon-carbon triple bonds strengthen a solid's matrix and generate additional free space (a nanometer scale pore space), thereby lowering the k value of the solid's dielectric constant. Thus, in one aspect, the present invention provides CDO films including at least some carbon-carbon triple bonds and their derivative forms. These derivative forms of triple bonds include carbon-carbon double bonds, carbon-carbon single bonds, and their crosslinked forms with other compositional atoms, including Si, O, C and H, in a CDO film. As discussed below, the incorporation of carbon-carbon triple bond in the CDO film can be detected using, for example, Fourier Transformation Infrared (FTIR) spectrometry. The content of carbon-carbon triple bond in the CDO film can be quantitatively described by the ratio of its FTIR peak area centered at $\sim 2100\text{ cm}^{-1}$ to the FTIR peak area of main backbone Si-O-Si matrix centered at $\sim 1020\text{ cm}^{-1}$. Preferably, the ratio of FTIR $\text{C}\equiv\text{C}$ triple bond peak area to Si-O bond peak area will fall in the range of about 0.05% to 20%, more preferably in the range of about 0.3% to 7%.

[0024] The advantages gained by introducing these unsaturated groups can be understood as follows. There are four major structural configurations for carbon in CDO films. By way of illustration, Figure 1 illustrates these configurations. The sp^3 structure 100 has the most degrees of freedom while the other three formats (sp^2 format 102 and sp formats 104 and 106) have fewer degrees of freedom and thus have more rigidity. Due to the reactive nature of deposition process and carbon-carbon

triple bonds, not only triple bonds themselves but also their derivative forms will be present in CDO films. These derivative forms result from the opening of one or two of the triple bond to form carbon-carbon double bond or carbon-carbon bond, and/or crosslinking to Si-O-Si network. The sp^2 and sp structures comprise C=C or C≡C bonds and have significantly different atom-atom of distance than C-C, C-O, Si-O, or Si-C bonds do. Nominal bond length of C-C bond is ~1.5 Angstroms, that of C=C bond is ~1.3 Angstroms and that of C≡C bond is ~1.2 Angstroms, that of C-O bond is ~1.1 Angstroms while the nominal bond length of Si-O bond is ~1.6 Angstroms and that of Si-C bond is ~1.9 Angstroms. Because of their rigidity and bond lengths, the C=C or C≡C bonds (and their derivative forms) provide means to alter the Si-O-Si matrix structure and to engineer the lattice structure of CDO films in order to lower the stress commonly associated with the CDO film and increase the nanometer scale pore space in the CDO matrix.

[0025] The total residual stress of the CDO films produced using these precursors and methods (precursor and/or process optimization) is preferably less than about 50 MPa tensile stress, and more preferably less than about 30 MPa tensile stress. It has also been demonstrated that the resulting film may have a compressive stress rather than a tensile stress (which is usually shown as a negative number). If the film exhibits a net intrinsic compressive stress, the magnitude of that compressive stress is preferably less than about -25 MPa, and more preferably less than -20 MPa compressive. One suitable apparatus used to measure internal stress is the “Flexus” tool purchased from KLA-Tencor Corporation. But any tool that accurately measures bow or other deviation from planarity in a wafer can be employed.

[0026] The films preferably possess a variety of other mechanical properties rendering them suitable for integration in demanding IC fabrication processes. Examples of such other mechanical properties include hardness, modulus, blanket film cracking limit, fracture toughness (resistance to crack propagation after a crack is initiated) and cracking propagation velocity. Hardness and modulus are well defined within the art and will not be discussed in detail herein. Measures of film hardness and modulus presented herein may be made with any suitable apparatus including a nano-indentation device. In the context of the present invention, a desirable modulus range is higher than about 3 GPa, most preferably higher than about 6 GPa

[0027] One manifestation of residual tensile stress in a film is cracking. A film's cracking threshold is a measure of the thickness of the film on a blank substrate (e.g., a flat 200 mm wafer) that can be deposited without forming a crack. In a typical experiment, the dielectric film is deposited to various thicknesses using a single set of process conditions. The resulting wafer (with dielectric layer) is set aside without disturbance for a period of time (e.g., one day) and examined for cracks. The greatest thickness at which no crack is observed is the cracking threshold. For many processes, the cracking threshold is measured in μm . For the purposes of this invention, the cracking threshold is greater than about 3 μm . Most preferably, the cracking threshold is greater than about 5 μm .

[0028] Another physical property of relevance to the CDO film is its refractive index, an indication of how much carbon related bonds are in the film. This value has a bearing on the etch sensitivity of the resulting film. For many applications, it is desired that the CDO film be relatively easy to etch relative to the barrier or etch stop layer used together with CDO film during the IC fabrication. In this regard, the refractive index of CDO film should be at most about 1.6. More preferably, it is at most about 1.55 (e.g., between about 1.3 and 1.5.). Refractive index can be measured by many types of optical inspection tools, including ellipsometers and reflectometers.

[0029] Note that the CDO films described in this application are composed of, at least, silicon, oxygen, hydrogen, and carbon. The typical chemical composition of the as deposited CDO films includes 10-25 atomic percentage silicon, 10-60 atomic percentage oxygen, 10-50 atomic percentage carbon and 20-35 atomic percentage of hydrogen. In some embodiments, other elements may be present in the CDO films.

[0030] Figure 2 is a flowchart illustrating at a high level one methodology for creating low-k (a dielectric constant of below about 2.7) CDO dielectric layers in accordance with this invention. In a step 205 a wafer is supplied. In step 210, one or more precursors are introduced. Precursors are chosen to have a high carbon content and, in some embodiments, one or more double bonds or triple bonds. In step 215, plasma is ignited under conditions that promote incorporation of desired compositional bond structure in the CDO film. Selection of precursors employed in step 210 is detailed in the Precursor Optimization section below. Step 215 is described in detail in the Process Optimization section, also below.

PRECURSOR OPTIMIZATION

[0031] Both process optimization and precursor selection can have strong effects on the material properties of the film. Precursors of interest should be carbon rich and contain some degree of unsaturation (e.g., at least one carbon-carbon triple bond or double bond). Generally, carbon may be provided in the form of alkyl groups, alkene groups, and alkyne groups for example. For many applications, it will be desirable to choose at least one precursor that has at least two carbon-silicon bonds per silicon atom. Precursors having any of these enumerated properties may be used alone (in a process gas having a single precursor) or in combination with other precursors

[0032] Examples of principal precursors for CDO dielectrics of this invention include silane (in combination with a carbon containing precursor), alkylsilanes (e.g., trimethylsilane and tetramethylsilane), alkoxysilanes (e.g., methyltriethoxysilane (MTEOS), methyltrimethoxysilane (MTMOS) diethoxymethylsilane (DEMS), methylmethoxysilane (MDMOS), trimethylmethoxysilane (TMMOS) and dimethyldimethoxysilane (DMDMOS)), linear siloxanes (e.g., diethoxymethylsilane), cyclic siloxanes (e.g. alkylcyclotetrasiloxanes such as octamethylcyclotetrasiloxane (OMCTS) and tetramethylcyclotetrasiloxane (TMCTS)), and various compounds with silyl groups. Note that one example of a silane is di-*tert*-butylsilane. In each class of compounds, the precursor may be entirely saturated or it may include one or more carbon-carbon triple bonds or double bonds. If the precursor is entirely saturated, then the process gas will require a secondary precursor that contains carbon-carbon double bonds or carbon-carbon triple bonds.

[0033] Precursors having carbon-carbon triple bonds or double bonds may be found in various classes of compound including, for example, silanes having at least one hydrocarbon group with a carbon-carbon double bond and at least one alkyl group or at least one oxy-hydrocarbon group, silanes having at least one hydrocarbon group with a carbon-carbon triple bond and at least one alkyl group or at least one oxy-hydrocarbon group, bis(alkylsilyl) acetylenes, bis(alkylsilyl) ethylenes, and siloxanes having pendant hydrocarbon groups with a carbon-carbon triple bond or double bond. Several silicon-containing hydrocarbons (with or without oxygen) have been

identified as potential precursors that may be used in a deposition process to form CDO films having low dielectric constants. These include the following:

Ethynyltrimethylsilane ($\text{SiC}_5\text{H}_{10}$): ETMS, also known as trimethylsilaneacetylene (TMSA), $(\text{CH}_3)_3\text{Si}-\text{C}\equiv\text{C}-\text{H}$

Propargyltrimethylsilane ($\text{SiC}_6\text{H}_{12}$): PTMS, $(\text{CH}_3)_3\text{Si}-\text{CH}_2-\text{C}\equiv\text{C}-\text{H}$

Propargyloxytrimethylsilane ($\text{SiC}_6\text{H}_{12}\text{O}$): POTMS, $(\text{CH}_3)_3\text{Si}-\text{O}-\text{CH}_2-\text{C}\equiv\text{C}-\text{H}$

Bis(trimethylsilyl)acetylene ($\text{Si}_2\text{C}_8\text{H}_{18}$): BTMSA, $(\text{CH}_3)_3\text{Si}-\text{C}\equiv\text{C}-\text{Si}(\text{CH}_3)_3$

Bis(trimethylsilyl)methylene ($\text{Si}_2\text{C}_7\text{H}_{20}$): BTMSM, $(\text{CH}_3)_3\text{Si}-\text{CH}_2-\text{Si}(\text{CH}_3)_3$

Bis(trimethylsilyl)ethylene ($\text{Si}_2\text{C}_8\text{H}_{22}$): BTMSE, $(\text{CH}_3)_3\text{Si}-\text{CH}_2-\text{CH}_2-\text{Si}(\text{CH}_3)_3$

1,3-Diethynyltetramethyldisiloxane ($\text{Si}_2\text{C}_8\text{H}_{14}\text{O}$): DTDS, $\text{HC}\equiv\text{C}-\text{Si}(\text{CH}_3)_2-\text{O}-\text{Si}(\text{CH}_3)_2-\text{C}\equiv\text{C}-\text{H}$

1,3-Divinyltetramethyldisiloxane ($\text{Si}_2\text{C}_8\text{H}_{18}\text{O}$): DVDS, $\text{H}_2\text{C}=\text{CH}-\text{Si}(\text{CH}_3)_2-\text{O}-\text{Si}(\text{CH}_3)_2-\text{CH}=\text{CH}_2$

Vinyltrimethylsilane ($\text{SiC}_5\text{H}_{12}$): VTMS, $(\text{CH}_3)_3\text{Si}-\text{CH}=\text{CH}_2$

Vinylmethyldimethoxysilane ($\text{SiC}_5\text{H}_{12}\text{O}_2$): VMDMOS, $(\text{CH}_3\text{O})_2(\text{CH}_3)\text{Si}-\text{CH}=\text{CH}_2$

Dimethylmethoxysilaneacetylene ($\text{SiC}_5\text{H}_{11}\text{O}$): DMMOSA, $(\text{CH}_3\text{O})(\text{CH}_3)_2\text{Si}-\text{C}\equiv\text{CH}$

Methyldimethoxysilaneacetylene ($\text{SiC}_5\text{H}_{11}\text{O}_2$): MDMOSA, $(\text{CH}_3\text{O})_2(\text{CH}_3)\text{Si}-\text{C}\equiv\text{CH}$

Dimethylethoxysilaneacetylene ($\text{SiC}_6\text{H}_{13}\text{O}$): DMEOSA, $(\text{C}_2\text{H}_5\text{O})(\text{CH}_3)_2\text{Si}-\text{C}\equiv\text{CH}$

Methyldiethoxysilaneacetylene ($\text{SiC}_7\text{H}_{15}\text{O}_2$): MDEOSA, $(\text{C}_2\text{H}_5\text{O})_2(\text{CH}_3)\text{Si}-\text{C}\equiv\text{CH}$

Ethyldiethoxysilaneacetylene ($\text{SiC}_8\text{H}_{17}\text{O}_2$): EDEOSA, $(\text{C}_2\text{H}_5\text{O})_2(\text{C}_2\text{H}_5)\text{Si}-\text{C}\equiv\text{CH}$

Dimethylsilane-diacetylene (SiC_6H_8): DMSDA, $(\text{CH}_3)_2\text{Si}(\text{C}\equiv\text{CH})_2$

Divinyldimethylsilane ($\text{SiC}_6\text{H}_{12}$): DVDMS, $(\text{CH}_3)_2\text{Si}(\text{CH}=\text{CH}_2)_2$

Methylsilane-triacetylene (SiC_7H_6): MSTA, $(\text{CH}_3)\text{Si}(\text{C}\equiv\text{CH})_3$

Tetraacetylene Silane (SiC_8H_4): TAS, $\text{Si}(\text{C}\equiv\text{CH})_4$

[0034] The functional groups are $\text{C}=\text{C}$ (double bonds) and $\text{C}\equiv\text{C}$ (triple bonds) which may be pendant or embedded within other functionalities. Preferably, the desired functional group in the precursor(s) is the $\text{C}\equiv\text{C}$ (triple bonds). During deposition, these special functional groups become integrated in the CDO film on the substrate. Rigid $\text{C}\equiv\text{C}$ and/or $\text{C}=\text{C}$ bonds, and their derivative bonding structures through crosslinking with Si, O, and C, when embedded in the CDO film, strengthen the material matrix and alter Si-O-Si backbone structure of CDO films, resulting in a more rigid lattice, thus lowering the tensile stress of the CDO film. As presented below, the incorporation of $\text{C}=\text{C}$ and $\text{C}\equiv\text{C}$ bond and their derivative forms within the Si-O-Si structure was observed by FTIR and other analytical methods. As mentioned, such films may be formed from a single carbon-containing precursor or multiple precursors in combination. Obviously, if a single precursor is used, then it must contain at least one carbon-carbon triple or double bond. But if multiple precursors are used in combination, it is not necessary for each of them to include an unsaturated group. Various primary precursors may be employed which have no double bonds or triple bonds.

[0035] Examples of secondary precursors include relatively small molecules having 2 to 6 carbon atoms and one or more carbon-carbon double bonds or carbon-carbon triple bonds. Specific examples include C_3H_4 : $\text{CH}_3\text{-C}\equiv\text{C-H}$, C_2H_2 : $\text{H-C}\equiv\text{C-H}$, C_2H_4 : $\text{CH}_2=\text{CH}_2$, C_3H_6 : CH_2CHCH_3 , C_3H_4 : $\text{CH}_2=\text{C}=\text{CH}_2$, Cyclopropene (H_2CCHCH), 1,3,5-Hexatriene (C_6H_8 - $\text{CH}_2=\text{CH}:\text{CH}=\text{CH}:\text{CH}=\text{CH}_2$), and 2-Methyl-1-buten-3-yne (C_5H_6 - $\text{CH}_2=\text{C}(\text{CH}_3):\text{C}\equiv\text{C-H}$). Other potential candidates for secondary precursors are silicon-containing hydrocarbons, or oxygen-containing hydrocarbons.

[0036] The precursor, in liquid or gaseous form, is but one component of the process chemicals employed during deposition. The process chemicals are those gases or liquids introduced into a reactor, such as a chemical vapor deposition (CVD) reactor, to allow deposition of the CDO film. Generally, the process gases will

include at least a carrier gas and one or more precursor gases/liquids introduced to the reaction chamber via the carrier gas. At least one of the precursors or the carrier gas should act as a source of oxygen. The source of silicon usually comes from a precursor gas/liquid. The hydrocarbon groups for the CDO film (including groups containing carbon-carbon double bonds and triple bonds) may come from either the precursor chemical(s) or the carrier gas, as indicated.

[0037] Generally, the carrier gas is provided in much greater volumes than the precursor gases. It is used as a delivery vehicle and a means for sweeping precursor materials and byproducts through the reactor. Various oxygen containing gases such as molecular oxygen (O_2), ozone (O_3), hydrogen peroxide (H_2O_2), nitrous oxide (N_2O) and carbon dioxide (CO_2) may be used. Carbon dioxide is preferred for many applications of this invention. In some embodiments hydrogen is used as the carrier gas. In still other embodiments, inert gases such as helium, argon, etc. are used. Examples of hydrocarbon carrier gases include acetylene (C_2H_2), ethylene (C_2H_4), propene ($CH_2=CHCH_3$), propyne ($CH_3C\equiv CH$), 1,2-propadiene ($CH_2=C=CH_2$), and Cyclopropene (H_2CCHCH).

[0038] In one example, the process gas employs a carrier gas but no separate oxygen source (e.g., molecular oxygen, ozone, hydrogen peroxide or carbon dioxide). Examples of the carrier gas include inert gases and hydrogen. In this example, a single precursor provides all the necessary oxygen, silicon, and carbon, including the carbon-carbon triple bonds and/or double bonds. As indicated, siloxanes and various silanes or compounds having silyl groups with hydrocarbon oxy moieties are suitable for this purpose.

[0039] In a second process gas example, the carrier gas again provides no oxygen. In this case, however, there are at least two precursor gases. The primary precursor provides oxygen, silicon, and some amount of carbon and hydrogen. Examples of such primary precursors includes TMCTS, DEMS, MTEOS and OMCTS. A secondary precursor is employed to provide the carbon-carbon triple bonds and/or double bonds. Note that in some cases, the carrier gas could be one of the secondary precursor hydrocarbons.

[0040] In a third process gas example, the carrier gas supplies some or all of the oxygen. As indicated, examples of suitable oxygenated carrier gases are carbon dioxide, ozone, hydrogen peroxide, molecular oxygen or other oxygen containing molecules. In this third example, only a single precursor is employed. It may or may not include oxygen. In cases where no oxygen is used, it could simply be a hydrocarbon silane material. Preferably, however it includes some degree of unsaturation. More preferably, the unsaturation involves one carbon-carbon triple bond. Examples of suitable precursors for this embodiment include ETMS or TMSA, PTMS, BTMSA, TAS, MSTA, MDEOSA, DMEOSA, DMSDA and VTMS. Any one of these "single precursors" may be used in conjunction with a carrier gas.

[0041] In a fourth example of a process gas, oxygen is again supplied in a carrier gas such as carbon dioxide, oxygen, ozone, nitrous oxide, or hydrogen peroxide. However, in this case two or more precursors are employed. At least one of these may be similar to those identified in the second example. However, it is not necessary for oxygen to be present in either the primary or secondary precursors. However, in some embodiments, some amount of oxygen may be present in one or more of these molecules. Many relatively simple hydrocarbon silanes and/or silyl compounds may be employed as the primary precursor.

PROCESS OPTIMIZATION

[0042] Various deposition techniques may be employed to form the CDO dielectric materials of this invention. These include various other forms of chemical vapor deposition (CVD) including plasma enhanced CVD (PECVD) and high-density plasma CVD (HDP CVD). HDP CVD of dielectric materials is described in various sources including US Patent Application No. 09/996,619, filed November 28, 2001 by Atiye Bayman et al. and titled "Gap Fill for High Aspect Ratio Structures", which is incorporated herein by reference for all purposes. Additionally, other techniques such as spin on techniques and deposition from supercritical solutions may be employed. But for many applications of this invention, a plasma based CVD process is employed.

[0043] Further the deposition conditions may be optimized to promote the crosslinking of incorporated bonds. Without this crosslinking, the film mechanical strength will generally be low due to the fact that an increase in content of methyl group CH_3 as a terminating group in the CDO film will reduce the bonding density per volume thus the bonding integrity of the film. With crosslinking, the Si-O-Si matrix structure is strengthened. As a result, the mechanical strength, or the fracture toughness, of the as deposited CDO film will be high.

[0044] Compositional bonds formed in CDO film of particular interest to this invention include Si- CH_2 -Si, Si- $\text{C}\equiv\text{C}$ -Si, Si- $\text{CH}=\text{CH}$ -Si, Si- $\text{CH}_2\text{-CH}_2$ -Si and other derivatives of these bonds due to Si, C or O crosslinking, such as Si-O- $\text{C}\equiv\text{C}$ -Si, Si-O- $\text{CH}=\text{CH}$ -Si, Si-C(-H,-OSi)- CH_2 -Si, etc. It is noted that the chemical bond length and angle varies with the degree of saturation and crosslinking. Nominal bond length of the C-C bond is $\sim 1.5 \text{ \AA}$, that of the C=C bond is $\sim 1.3 \text{ \AA}$, that of the $\text{C}\equiv\text{C}$ bond is $\sim 1.2 \text{ \AA}$, and that of the C-O bond is $\sim 1.1 \text{ \AA}$ while the nominal bond length of the Si-O bond is $\sim 1.6 \text{ \AA}$ and that of the Si-C bond is $\sim 1.9 \text{ \AA}$. It is evident that the incorporation of $\text{C}\equiv\text{C}$ bond and its derivatives (C=C, C-C) and their crosslinking within the CDO film will greatly influence the Si-O-Si matrix structure. More specifically, the Si-O-Si bond angle will change significantly as the desired C related bonds are incorporated and crosslinked. Since the Si-O-Si matrix is the backbone structure of the CDO film, the change in Si-O-Si bond angle will increase the nanometer scale pore space in the matrix and thereby decrease the dielectric constant in the matrix.

[0045] As discussed above, residual stress can be reduced by incorporating $\text{C}\equiv\text{C}$ bonds and its derivatives and promoting cross-linking/bridging in the CDO film. Due to the very reactive nature of carbon-carbon triple bond, there is abundant incorporation of $\text{C}\equiv\text{C}$ bond in the as deposited CDO film. To further enhance its incorporation and its crosslinking within the CDO film, one method is to increase ion bombardment during the PECVD deposition. Process conditions that increase ion bombardment may be chosen to increase one or both of (a) the mean energy of ion striking the substrate and (b) the flux of ions reaching the substrate. Physically, these results may be achieved by selecting process conditions that accomplish one of the following: (i) increasing the mean free path of the ions in the plasma, (ii) reducing the

distance that an ion must travel before striking the substrate, and (iii) increasing the mean energy or momentum of the ions that strike the substrate surface.

[0046] To increase the momentum or energy of ions striking the substrate surface, at least two different process conditions may be manipulated. First, using a dual-frequency reactor of the type described below, one can increase the relative amount of the low frequency component of the RF energy supplied to the reactor. This has the effect of increasing the length of time in a given oscillation during which ions are accelerated in a single direction (toward the wafer surface). Because the ions are exposed to a field in this direction for a longer period of time, they can accelerate to higher speeds and hence strike the substrate with greater momentum. Second, one can pulse the high frequency component of the RF power to accomplish a similar result.

[0047] As is well known in the art, in general, high frequency components of the RF power delivered to a reactor control the plasma density and low frequency components produce ion bombardment of the film. The high and low frequency components can be provided at any of a number of suitable frequencies. In a typical process, the LF component is provided in a frequency range of about 100 to 600kHz, more preferably about 200-500kHz, for example about 300kHz. The High Frequency HF component is generally between 2-60MHz — in one process example, an HF frequency of 13.156 MHz is used.

[0048] In one embodiment, the low frequency component of delivered RF power is between about 0 and 90 percent of the total power, and more preferably between about 0 and 60 percent of the total power (e.g., between about 5 and 40 percent). The optimal value will vary depending upon the mean free path of the ions and the various conditions that impact mean free path. In a specific example, the total power delivered is about 800 Watts on 6 200 mm wafers or 0.42 W/cm^2 in area density. This value can be varied depending upon the specific application and plasma reactor employed. In many cases, the low frequency component has a power area density of between about 0 W/cm^2 and 20 W/cm^2 , and more preferably between 0 W/cm^2 and 1 W/cm^2 .

[0049] In addition to varying the ratio of HFRF to LFRF, the HFRF power may be pulsed at a certain duty cycle, for example pulsing at between 500Hz and 10kHz and varying the HFRF duty cycle from 20-80%. This effectively superimposes a low frequency component on the plasma generation power.

[0050] Another method that may be used to increase ion bombardment during film deposition is to alter the deposition pressure. This simply increases the mean free path of ions in the deposition chamber. In one embodiment of the invention the deposition pressure is maintained at a pressure of between about 0.5 to 20 Torr, more preferably in the range of about 2-7 Torr.

[0051] Still another adjustment that may be used involves varying the gap between the two capacitor plates of the plasma reactor. In the apparatus described below, this involves choosing an appropriate gap between the showerhead (one capacitor plate) and a thermal block (a second capacitor plate) on which the wafer is positioned, thereby reducing the distance between the plasma source and the substrate. This reduces the distance that an ion must travel before striking the substrate. The ideal gap depends on the type of reactor employed and the process conditions. For many situations, the gap is preferably between about 3 and 20 millimeters.

[0052] Process optimization also includes setting the proper flow rates of the various compounds in the process gases. Note that the flow rates are chosen depending upon the amount of surface area to be covered. One can scale the flow rates chosen depending upon variations in the area to be deposited, including in situations where the reactor employs fewer or greater number of wafers and possibly employs 300 millimeter wafers as opposed to 200 millimeter wafers. For example, in experiments where six 200 millimeter wafers were used, the total precursor flow rate was 0.5 ml/min to about 10 ml/min. Note that this comprises the total flow rate of all precursors.

[0053] The deposition temperature can be tailored to meet the application. For some IC fabrication applications involving copper lines, for example, temperatures below 425 C may be required for intermetal dielectric deposition. In some

embodiments, the substrate temperature is maintained between about 300 and 425C (preferably between about 300 and 350C) during CDO film deposition.

EXPERIMENTAL

[0054] Various additional experiments were conducted to confirm aspects of this invention. Some of these are presented below.

[0055] Raman analysis of CDO films has been done. Figure 3a is a TMCTS and Figure 3b is a BTMSA based film. As explained, TMCTS is a cyclic tetrasiloxane without any double or triple bonds and BTMSA is a bis(silyl)acetylene. The two films are characterized by strong sharp peaks at 2910 and 2970 cm^{-1} , typical for symmetric and antisymmetric stretching of CH_3 groups in $-\text{Si}-\text{CH}_3$ structure, typical for silicones. The band at ~ 1418 in both spectra may be related with scissoring of $-\text{CH}_3$ groups. Figure 3a (the TMCTS based film) has a peak at 790 cm^{-1} that is due to Si-C stretching similar to the same band in SiC (a transversal optical (TO) band) and silicones. This peak was weak in Figure 3b (the BTMSA based film), at 796 cm^{-1} . A peak at 2100~2245 cm^{-1} in Figure 3a is likely due to Si-H stretching. Figure 3b has a band at 1608 cm^{-1} due to $-\text{C}=\text{C}-$ stretching, which was not detected in the TMCTS based film. A peak in Figure 3b at ~ 2250 cm^{-1} is probably due to $-\text{C}\equiv\text{C}-$ originating in the BTMSA precursor. These results show that there are $-\text{C}=\text{C}-$ and $-\text{C}\equiv\text{C}-$ bonds in the BTMSA based film, which is consistent with FTIR results. It is believed that the $-\text{C}=\text{C}-$ and $-\text{C}\equiv\text{C}-$ bonds take a key role in lowering CDO residual stress. In Figure 3a, bands at 494 and 621 cm^{-1} are due to $-\text{Si}-\text{O}-\text{Si}-$ vibrations. They probably are shifted in Figure 3b at 525 and 640 cm^{-1} , although the assignment of these bands is not certain.

[0056] Figure 4A shows FTIR spectra of ETMS, OMCTS and OMCTS+ETMS films, illustrating the chemical structure of the CDO matrix. The FTIR spectra of three CDO films exhibit an absorption peak corresponding to C-H stretch around 2900 to 3000 cm^{-1} . For CH_3 , the symmetric and asymmetric stretches are expected at 2964-2967 and 2907-2909 cm^{-1} respectively.

[0057] For methylene groups (CH_2), 2933 and 2878 cm^{-1} is assigned as the symmetric and asymmetric stretches, respectively. CH_3 symmetric and CH_2 asymmetric stretches were observed for all three films at 2955 and 2878 cm^{-1} , respectively. The $\text{-C}\equiv\text{C-}$ stretching band for the ETMS and OMCTS+ETMS films was observed at 2115 and 2120 cm^{-1} , respectively, which suggests that a significant amount of carbon triple bonds were incorporated into the CDO matrix after plasma polymerization. There is no $\text{-C}\equiv\text{C-}$ stretching band for OMCTS film but it contains two Si-H stretching bands, which are $(\text{SiO})_3\text{Si-H}$ and $(\text{CH}_3)(\text{SiO})_2\text{Si-H}$, observed at 2214 cm^{-1} and 2150 cm^{-1} , although they are very weak. The middle peaks around 1250-1280 cm^{-1} in the FTIR spectra of all three films in Figure 4A are assigned as the $\text{Si-(CH}_3)_x$ methyl rocking bands at 1270 cm^{-1} for OMCTS film and 1260 cm^{-1} for ETMS and OMCTS+ETMS films. The Si-O stretching bands for all three films were observed at 1022 cm^{-1} . The FTIR spectra of all three films also show SiC stretching bands at 796, 873, and 821 cm^{-1} . Other peaks related to derivative bonds from the C-C triple bond are also observed from the ETMS based CDO films. These bonds include: Si- $\text{CH}_2\text{-CH}_2\text{-Si}$ (1160 cm^{-1} and 1270 cm^{-1}), C=C (1620 – 1680 cm^{-1}), and CC (2100-2260 cm^{-1}).

[0058] Figure 4B shows the FTIR spectra of the following OSG films: (a) TMCTS (1 sccm) as precursor, and (b) TMCTS (1 sccm) and ETMS (0.4 sccm) as precursors. The results are similar to those observed in Figure 4A. Again, the FTIR spectra of the OSG films exhibit an absorption peak corresponding to C-H stretch around 2900 to 3000 cm^{-1} . For CH_3 , the symmetric and asymmetric stretches are expected at 2964-2967 and 2907-2909 cm^{-1} respectively. For methylene groups (CH_2), 2933 and 2878 cm^{-1} is assigned as the symmetric and asymmetric stretches, respectively. CH_3 symmetric and asymmetric stretches were observed for both films (TMCTS and TMCTS+ETMS) at 2908 and 2968 cm^{-1} , respectively. The absence of Si-C \equiv C-H stretching around 3300 cm^{-1} indicates that the terminal $\text{-C}\equiv\text{C-H}$ groups may be connected to the OSG matrix through cross-linking. Two Si-H stretching bands, which are $(\text{SiO})_3\text{Si-H}$ and $(\text{CH}_3)(\text{SiO})_2\text{Si-H}$, were observed at 2233 cm^{-1} and 2169 cm^{-1} although they are very weak for both films. The $\text{-C}\equiv\text{C-}$ stretching band, normally in the range of 2040-2100 cm^{-1} , was too weak to identify in the sample. The middle peaks around 1250-1280 cm^{-1} in the FTIR spectra of TMCTS and TMCTS+ETMS films in Figure 4B are assigned as the $\text{Si-(CH}_3)_x$ methyl rocking

bands at 1273 and 1263 cm^{-1} , respectively, which are also shown in the inset of Figure 4B. It is clear that the methyl rocking band at 1273 cm^{-1} , which is from $(\text{SiO})_3\text{Si-CH}_3$, is much stronger than the methyl rocking band at 1263 cm^{-1} , which is from $(\text{SiO})_2\text{Si-(CH}_3)_2$. The Si-O stretching bands for both films were observed at 1049 cm^{-1} . The FTIR spectra of TMCTS and TMCTS+ETMS films also show SiC stretching bands at 896, 850, 803 and 781 cm^{-1} , which are from $\text{Si(CH}_3)_2$, $\text{Si(CH}_3)_3$, $\text{Si(CH}_3)_2$ and $\text{Si(CH}_3)$, respectively.

[0059] Figure 5 shows the effect of BTMSA flow rate on dielectric constant. The data in this figure was taken from films deposited in Sequel® PECVD Chamber, Novellus Systems, Inc. The deposition process was conducted with high frequency RF power of 850 W, a pressure of 7.5 Torr, and a process gas comprising CO_2 at 5500 sccm, TMCTS at 1 sccm and BTMSA at the flow rates indicated in the figure. As shown, the dielectric constant decreases rapidly with increasing flow rate of BTMSA in the low flow rate range as shown in Figure 5, a behavior very similar to that observed for ETMS. Of particular note is the range of 0.25-0.70 sccm BTMSA flow rate. As seen, the dielectric constant increases slightly with increasing flow rate of BTMSA, which could be attributed to the fewer voids and/or higher density in the deposited films when BTMSA flow rate is higher than about 0.4 sccm.

[0060] Figure 6 presents the effect of pressure on dielectric constant. Again deposition was conducted in a Sequel® PECVD Chamber. As shown, the dielectric constant decreases with increasing pressure. The increase in deposition pressure increases the precursor concentration exposed to the substrate and reduces the reaction rate. The reduction in reaction rate increases degree of incorporation of CC triple bonds in the CDO film. This increases the fractional volume of nano voids in the film and lowers the dielectric constant of the CDO film.

[0061] Various additional examples will now be presented. These show recipes which yield k value < 2.60 (for the first 4 examples) based on KLA-Tencor (San Jose, California) F5 thickness measurement and a Hg probe. In all cases, deposition was conducted in a Sequel® PECVD Chamber.

[0062] **Example 1** - Plasma was generated with a HFRF (high frequency) power of 750 W during CVD polymerization. LFRF (low frequency) power was set to 0 W.

The gas mixture included TMCTS at flow rate of 1 ccm, ETMS at flow rate of 0.4 ccm and CO₂ at flow rate of 5500 sccm. The chamber pressure was kept at 7.5 Torr. The film had a dielectric constant of 2.60 for the as-deposited conditions. Process repeatability is illustrated in Figure 7, indicating that dielectric constant can be reproducible at $k=2.60\pm0.01$.

[0063] **Example 2** - In this example, the plasma was operated at a HFRF power of 800 W, LFRF power at 0 W and a chamber pressure of 8.5 Torr was used. A gas mixture of TMCTS flow rate of 1 ccm, ETMS flow rate of 0.4 ccm and CO₂ flow rate of 4500 sccm was used during CVD polymerization. The as-deposited film had a dielectric constant of 2.58.

[0064] **Example 3** - In this example, the plasma was operated at an RF power of 800 W with a chamber pressure of 11.5 Torr. A gas mixture of TMCTS flow rate of 1 ccm, ETMS flow rate of 0.4 ccm and CO₂ flow rate of 5500 sccm was used during CVD polymerization. The as-deposited film had a dielectric constant of 2.54.

[0065] **Example 4** - In this example, a different secondary precursor was used for this process. The plasma was operated at a HFRF power of 850 W, LFRF of 0 W with a chamber pressure of 7.5 Torr. A gas mixture including TMCTS flow rate of 1 ccm, BTMSA flow rate of 0.4 ccm and CO₂ flow rate of 5500 sccm was used during CVD polymerization. The as-deposited film had a dielectric constant of 2.59.

[0066] **Example 5** - In this example, the HFRF power was set at 1200W, and the LFRF at 300W, in a Sequel chamber. A chamber pressure of 7 Torr was used in this process. The gas mixture of BTMSA flow rate of 2.0 ccm and CO₂ flow rate of 3000 sccm was used during PECVD deposition at 350C. The as-deposited film had a dielectric constant of 2.69 and a low tensile stress of 24MPa. The critical cracking thickness of this film was $>5\ \mu\text{m}$.

[0067] **Example 6.** In this example, the HF RF power was set at 1000W and no LF RF power was used in a Sequel® chamber. A chamber pressure of 7 Torr was used in this process. The gas mixture of ETMS flow rate of 1.5 ccm and CO₂ flow rate of 4000 sccm was used during PECVD deposition at 400C. The as-deposited film had a dielectric constant of 2.61 and stress of 35.55Mpa (tensile). The critical cracking thickness of this film is $3\ \mu\text{m}$.

[0068] Example 7 - In this example, the HF RF power was set at 3000W and LF RF power at 200W in a Novellus Vector® chamber which can be used to deposit films on four 300mm wafers simultaneously. A chamber pressure of 5.5 Torr was used in this process. The gas mixture of TMSA flow rate of 2.5 ccm, CO₂ flow rate of 4000 sccm and O₂ flow rate of 200sccm was used during PECVD deposition at 400C. The as-deposited film had a refractive index (RI) of 1.45, a dielectric constant of 2.71 and stress of 43 Mpa (tensile). The critical cracking thickness of this film is >5 µm.

APPARATUS

[0069] The present invention can be implemented in many different types of apparatus, such as chemical vapor deposition (CVD) reactors and spin-coating systems. Generally, the apparatus will include one or more chambers or “reactors” (sometimes including multiple stations) that house one or more wafers and are suitable for wafer processing. Each chamber may house one or more wafers for processing. The one or more chambers maintain the wafer in a defined position or positions (with or without motion within that position, e.g. rotation, vibration, or other agitation). In one embodiment, a wafer undergoing dielectric deposition is transferred from one station to another within the reactor during the process. While in process, each wafer is held in place by a pedestal, wafer chuck and/or other wafer holding apparatus. For certain operations in which the wafer is to be heated, the apparatus may include a heater such a heating plate. In a preferred embodiment of the invention, a PECVD (Plasma Enhanced Chemical Vapor Deposition) system, but other forms of CVD may be used as well, for example a HDP CVD (High Density Plasma Chemical Vapor Deposition) system.

[0070] Figure 8 provides a simple block diagram depicting various reactor components arranged for implementing the present invention. As shown, a reactor 800 includes a process chamber 824, which encloses other components of the reactor and serves to contain the plasma generated by a capacitor type system including a showerhead 814 working in conjunction with a grounded heater block 820. A high-frequency RF generator 802 and a low-frequency RF generator 804 are connected to a matching network 806 that, in turn is connected to showerhead 814. The power and

frequency supplied by matching network 806 is sufficient to generate a plasma from the process gas, for example 800W total energy.

[0071] Within the reactor, a wafer pedestal 818 supports a substrate 816. The pedestal typically includes a chuck, a fork, or lift pins to hold and transfer the substrate during and between the deposition reaction. The chuck may be an electrostatic chuck, a mechanical chuck or various other types of chuck as are available for use in the industry and/or research.

[0072] The process gases are introduced via inlet 812. Multiple source gas lines 810 are connected to manifold 808. The gases may be premixed or not. Appropriate valving and mass flow control mechanisms are employed to ensure that the correct gases are delivered during the deposition and plasma treatment phases of the process. In case the chemical precursor(s) is delivered in the liquid form, liquid flow control mechanisms are employed. The liquid is then vaporized and mixed with other process gases during its transportation in a manifold heated above its vaporization point before reaching the deposition chamber.

[0073] Process gases exit chamber 800 via an outlet 822. A vacuum pump 826 (e.g., a one or two stage mechanical dry pump and/or a turbomolecular pump) typically draws process gases out and maintains a suitably low pressure within the reactor by a close loop controlled flow restriction device, such as a throttle valve or a pendulum valve.

APPLICATIONS

[0074] This invention broadly applies to deposition of low-k low residual stress CDO dielectric material on any type substrate. In many cases, however, the CDO dielectric material will be used in integrated circuits or other electronic devices. A preferred use for the CDO films of this invention is for interlayer dielectric (ILD) applications (including both interlevel dielectrics (between active devices and the first metallization layer and intermetal dielectrics (“IMD” between adjacent metallization layers)). In these applications, the CDO films serve to replace conventional silicon dioxide or fluorinated silica glass (FSG) materials. Examples of non-ILD applications

include barrier and etch-stop (ES) layers, antireflective layers (ARL), hardmask layers, etc. In conventional systems, these layers are sometimes provided in the form of oxygen-doped carbides (which have a refractive index value of not greater than about 1.6.)

[0075] The ultimate thickness of a CDO dielectric film produced in accordance with this invention depends upon the application. For example, the final thickness for an interlayer dielectric or packaging application may range from 400 Angstroms to about 2 to 3 micrometers. In some cases, extra thickness is required to provide some amount of sacrificial dielectric to accommodate a subsequent planarization step.

[0076] In a preferred embodiment, the CDO films produced in accordance with this invention are used in multiple metallization layers. Such devices may have, for example, five or more metallization layers and five or more associated CDO films.

OTHER EMBODIMENTS

[0077] While this invention has been described in terms of certain embodiments, there are various alterations, modifications, permutations, and substitute equivalents, which fall within the scope of this invention. It should also be noted that there are many alternative ways of implementing the methods and apparatuses of the present invention. Further, there are numerous applications of the present invention, both inside and outside the integrated circuit fabrication arena. It is therefore intended that the following appended claims be interpreted as including all such alterations, modifications, permutations, and substitute equivalents as fall within the true spirit and scope of the present invention.